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QUALIFICATION: **VARIOUS**	
QUALIFICATION CODE: **VARIOUS**	LEVEL: **6**
COURSE: **PHYSICAL CHEMISTRY**	COURSE CODE: **PCH602S**
DATE: **JANUARY 2025**	SESSION: **1**
DURATION: **3 HOURS**	MARKS: **100**

SECOND OPPORTUNITY / SUPPLEMENTARY: EXAMINATION QUESTION PAPER

EXAMINER: ***Prof Habauka Kwaambwa***

MODERATOR: ***Dr Euodia Hess***

INSTRUCTIONS

1. Answer ALL the questions in Sections A and B.
2. Answer all questions on the separate answer sheet.
3. Please write neatly and legibly.
4. Do not use the left side margin of the exam paper. This must be allowed for the examiner.
5. No books, notes and other additional aids are allowed.
6. Mark all answers clearly with their respective question numbers.

PERMISSIBLE MATERIALS

Non-Programmable Calculator

ATTACHMENTS

List of Useful Constants and Equation

THIS QUESTION PAPER CONSISTS OF 7 PAGES (Including this front page and a list of useful constants and equation as an attachment)

SECTION A: MULTIPLE CHOICE QUESTIONS [20]

There are 10 questions in this section. Choose the correct answer. Each question carries 2 marks.

1. An ideal gas at 27°C is heated at constant pressure until its volume is double. The final temperature is:
   A. 54°C
   B. 327°C
   C. 108°C
   D. 654°C
   E. 600°C

2. Which of the following **is not** an intensive property?
   A. Pressure
   B. Temperature
   C. Density
   D. Heat
   E. Molar volume

3. A system does 430 J of work in its surroundings while absorbing 270 J of heat. Calculate the change in the internal energy of the system.
   A. 700 J
   B. 160 J
   C. −160 J
   D. 1600 J
   E. Insufficient Information

4. All of the following have a standard heat of formation value of zero at 25°C and 1.0 atm except:
   A. $N_2(g)$
   B. Fe(s)
   C. Ne(g)
   D. H(g)
   E. Hg(*l*)

5. Calculate the standard heat of formation, ΔH_f^o, for $FeS_2(g)$, given the following information:

   $2FeS_2(s) + 5O_2(g) \rightarrow 2FeO(s) + 4SO_2(g)$

   ΔH^o_{rxn} = - 1370 kJ

   ΔH^o_f for $SO_2(g)$ = - 297 kJ/mol

   ΔH^o_f for FeO(s) = - 268 kJ/mol

   A. – 177 kJ
   B. – 1550 kJ
   C. – 774 kJ
   D. – 686 kJ
   E. + 808 kJ

6. If $\Delta G^o < 0$, then K is _____. If $\Delta G^o > 0$, then K is _____. If $\Delta G^o = 0$, then K is _____.

   A. $> 1, < 1, = 1$
   B. $< 1, > 1, = 1$
   C. $< 0, > 0, = 0$
   D. $> 0, < 0, = 0$
   E. $< 1, > 1, = 0$

7. The $\Delta H_{\text{sublimation}}$ of I_2 is 60.46 kJ/mol, while its $\Delta H_{\text{vaporization}}$ is 41.71 kJ/mol. What is the ΔH_{fusion} of I_2?

   A. 102.17 kJ/mol
   B. – 102.17 kJ/mol
   C. 18.75 kJ/mol
   D. – 18.75 kJ/mol
   E. Insufficient information

8. When a conductance cell was filled with 0.0025 M solution of K_2SO_4, its resistance was 326 Ω. If the cell constant is 0.2281 cm^{-1}, the conductivity (in $\Omega^{-1}cm^{-1}$) of K_2SO_4 solution is

   A. 4.997×10^{-4}
   B. 5.997×10^{-4}
   C. 7.997×10^{-4}
   D. 3.997×10^{-4}
   E. 6.997×10^{-4}

9. Which of the following expressions is correct?

   A. $\Lambda_o\left(Al_2(SO_4)_3\right) = 3\lambda_o^+\left(Al^{3+}\right) + 2\lambda_o^-\left(SO_4^{2-}\right)$
   B. $\Lambda_o\left(Al_2(SO_4)_3\right) = \lambda_o^+\left(Al^{3+}\right) + \lambda_o^-\left(SO_4^{2-}\right)$
   C. $\Lambda_o\left(NH_4OH\right) = \Lambda_o\left(NH_4Cl\right) - \Lambda_o\left(NaCl\right) + \Lambda_o\left(NaOH\right)$
   D. $\Lambda_o\left(FeSO_4\right) = 2\lambda_o^+\left(Fe^{2+}\right) + 2\lambda_o^-\left(SO_4^{2-}\right)$
   E. $\Lambda_o\left(NH_4OH\right) = \Lambda_o\left(NH_4Cl\right) - \Lambda_o\left(NaOH\right) - \Lambda_o\left(NaCl\right)$

10. If the activation for the forward direction of an elementary step is 52 kJ and the activation energy in the reverse direction is 74 kJ, what is the enthalpy change od reaction for this step?
   A. 22 kJ
   B. – 22 kJ
   C. 52 kJ
   D. – 52 kJ
   E. 126 kJ

SECTION B **[80]**

There are **FIVE** questions in this section. Answer **all** Questions.

QUESTION 1 **[14]**

(a) State whether each of the following statements is **true** or **false**. If false either correct it or state briefly the reason for its being false.

(i) $w = \oint dw = 0$ and $\Delta H = \oint dH = 0$ (2)

(ii) The compressibility factor, $Z > 1$ for many gases at high pressures is attributed to finite size of gas molecules and repulsive forces. (2)

(iii) For a perfect crystalline substance, $S_{0^\circ C} = 0$. (2)

(iv) $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$ (2)

(v) According to Trouton's law, the entropy of vaporisation at normal boiling point of benzene (C_6H_6) and water is approximately equal to 88 $JK^{-1}mol^{-1}$. (2)

(b) Starting with $PV^{\gamma} =$ Constant, show that $TV^{\gamma-1} =$ Constant, where P, V and T is pressure, volume and absolute temperature, respectively, and g is the relationship between C_v and C_p. (4)

QUESTION 2 **[13]**

(a) State whether q, w, ΔU, ΔH and ΔS are positive, negative or zero in adiabatic compression of an ideal gas. (5)

(b) A sample consisting of 2.00 mol argon (assume to behave as ideal gas) is expanded reversibly and isothermally at 0°C from 22.4 dm^3 to 44.8 dm^3. For this process, calculate q, w ΔU and ΔH. (8)

QUESTION 3 **[13]**

(a) Estimate the enthalpy change of formation for $NH_3(g)$ at 100°C given: (3)

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g),\ \Delta H_f^\circ(25^\circ C) = -46.11\ kJmol^{-1}$$

$C_p(N_2, g) = 29.12\ JK^{-1}mol^{-1}$
$C_p(H_2, g) = 28.82\ JK^{-1}mol^{-1}$
$C_p(NH_3, g) = 35.06\ JK^{-1}mol^{-1}$

(b) Calculate ΔG^o for 1 mole of N_2O_4 decomposition at 298 K, given $K_p = 0.163$. If ΔS^o for the reaction is 184.2 $JK^{-1}mol^{-1}$ at 298 K, calculate ΔH^o at 298 K. (3)

(c) The equilibrium constant of the reaction

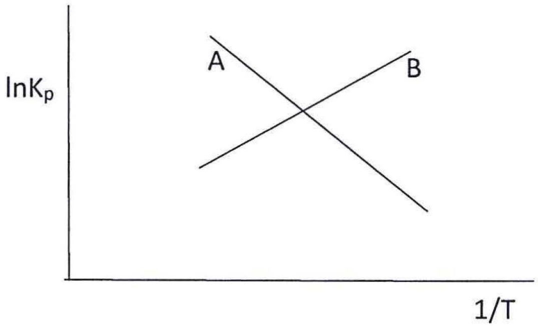
$COCl_2(g) \rightleftharpoons CO)g) + Cl_2(g)$

was determined as a function of temperature and the data was fitted using the linear form of the van't Hoff isochore and the result was:

$$\ln K_p = \frac{14080}{T} + 17.85$$

Use these results to obtain ΔH^o, ΔS^o and ΔG^o. (4)

(d) Is the reaction in (c) above endothermic or exothermic? Give a reason for you answer. Which linear plot A or B in the diagram below best represents this reaction? (3)



QUESTION 4 **[20]**

(a) Explain briefly why **conductivity, κ,** is not the most convenient quantity to use for the study of electrolytic conduction. (2)

(b) The molar conductivities at infinite dilution (in $\Omega^{-1}cm^2mol^{-1}$) of NaCl, HCOONa and HCl are 126.4, 104.6 and 426.1, respectively, at 25°C. The molar conductivity of the carboxylic acid, HCOOH, at a concentration of 0.100 M is 50.5 $\Omega^{-1}cm^2mol^{-1}$. Calculate the following:

(i) molar conductivity at infinite dilution, Λ_o, of HCOOH. (2)

(ii) dissociation constant K_a and the pH of the acid solution. (6)

(c) State the two functions of a salt bridge in an electrochemical cell. (2)

(d) Given the following electrochemical cell notation

$$\mathrm{Pt}\left|\mathrm{Ti}^{3+}(0.1\mathrm{m}),\mathrm{Ti}^{4+}(0.1\mathrm{m})\right|\left|\mathrm{Cu}^{+}(0.1\mathrm{m})\right|\mathrm{Cu(s)}$$

(i) Deduce the overall chemical reaction of the electrochemical cell. (2)

(ii) If the emf of the cell, E_{cell}, is 0.442 V at 25°C, calculate ΔG, ΔH and ΔS for the reaction if the temperature coefficient of the emf is – 1.25×10^{-4} VK^{-1} at this temperature. (6)

QUESTION 5 **[20]**

(a) What is the overall order of the reaction described by each of the rate expressions below? State the units of the rate coefficient of the rate is in moldm^{-3}s^{-1}.

(i) Rate = $k\frac{[A]^{1.5}}{[B]^{1.5}}$ (ii) Rate = $k[A][B]^{0.5}[C]^{1.5}$ (4)

(b) The reaction $H_2 + I_2 \rightarrow 2HI$ is first order with respect to $[H_2]$ and $[I_2]$. When $[H_2]$ = 1 molL^{-1} and $[I_2]$ = 2 molL^{-1}, the following kinetic are observed.

$\frac{d[HI]}{dt}$ = 1.78 x 10^{-4} molL^{-1}s^{-1} at 556 K and $\frac{d[HI]}{dt}$ = 0.2572 molL^{-1}s^{-1} at 700 K.

Calculate the rate constant at each of the temperatures and evaluate the activation energy [Assume that the pre-exponential factor is constant] (6)

(c) The reverse reaction, i.e. $2HI \rightarrow H_2 + I_2$, has an activation energy of 183 kJmol^{-1}. Does this make the reaction $H_2 + I_2 \rightarrow 2HI$ exothermic or endothermic? Explain your answer with a diagram of the energy profile of the reaction. (6)

(d) Hydrogen peroxide, H_2O_2, decomposes in water by a first order kinetics process. A 0.156 moldm^{-3} solution of H_2O_2 in water has an initial rate of 1.14 x 10^{-5} moldm^{3}s^{-1}. Calculate the rate constant, k, for the decomposition reaction and the half-life of the decomposition. (4)

END OF EXAM QUESTION PAPER

LIST OF USEFUL CONSTANTS AND EQUATION

Van der Waals eq$^{\underline{n}}$. $P = \dfrac{nRT}{V - nb} - \dfrac{n^2 a}{V^2} = \dfrac{RT}{\bar{V} - b} - \dfrac{a}{\bar{V}^2}$

Universal Gas constant	R	=	8.314 J K^{-1} mol^{-1}
Boltzmann's constant,	k	=	1.381×10^{-23} J K^{-1}
Planck's constant	h	=	6.626×10^{-34} J s
Debye-Hückel's constant,	A	=	0.509 $(mol\ dm^{-3})^{1/2}$ or $mol^{-0.5}kg^{0.5}$
Faraday's constant	F	=	96485 C mol^{-1}
Mass of electron	m_e	=	9.109×10^{-31} kg
Velocity of light	c	=	2.998×10^{8} m s^{-1}
Avogadro's constant	N_A	=	6.022×10^{23}
1 electron volt (eV)		=	1.602×10^{-19} J

1 atm = 101325 Pa = 760 mmHg = 760 torr; 1 bar = 10^5 Pa